LA-13182-SR
Status Report

94-1 Research and Development Project Lead Laboratory Support

Status Report

April 1 – June 30, 1996

Los Alamos
NATIONAL LABORATORY

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Program Manager: Randall Erickson
Project Leader: Mark Dinehart
Project Analyst: Nora Rink
Editor: Linda K. Wood, Group CIC-1
Photo Composition: Barbara A. Ritchie, Group CIC-1

Principal Investigators:
Moses Attrep, Pamela K. Benicewicz,
John M. Berg, Tom Blair,
Carol Burns, Darryl P. Butt,
Charles Brown, Steven Buelow,
Teresa Cremers, Lynn Foster,
Eduardo Garcia, Clinton Heiple,
Richard Hildner, David Horrell,
Gordon Jarvinen, Daniel J. Kathios,
Guy Lussiez, Horacio E. Martinez
Steven McKee, James McNeese,
David Morris, Timothy O. Nelson,
Ann Schake, Norman C. Schroeder,
Wayne Smith, Kirk Veirs,
Gerald Veazey, Mark A. Williamson,
Laura Worl, and Stanley Zygmunt

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Compiled by
Mark Dinehart

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT

Status Report
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ABSTRACT

This document reports status and technical progress for Los Alamos 94-1 Research and Development projects during the third quarter of FY96.

INTRODUCTION

This is the third status report published for Los Alamos National Laboratory 94-1 Research and Development Project Support. The Department of Energy Office of Environmental Management funds these projects in order to provide support for storage or disposal of legacy plutonium and of plutonium-bearing materials. These materials are the result of weapons production throughout the DOE complex. Descriptions and milestones for Los Alamos 94-1 Research and Development projects are found in report LA-UR-96-991, *94-1 Research and Development Project Lead Laboratory Support Technical Program Plan* (April 1996). Figure 1 presents the work breakdown structure for this effort. The present document reports status and technical progress for funded Los Alamos 94-1 R&D projects.

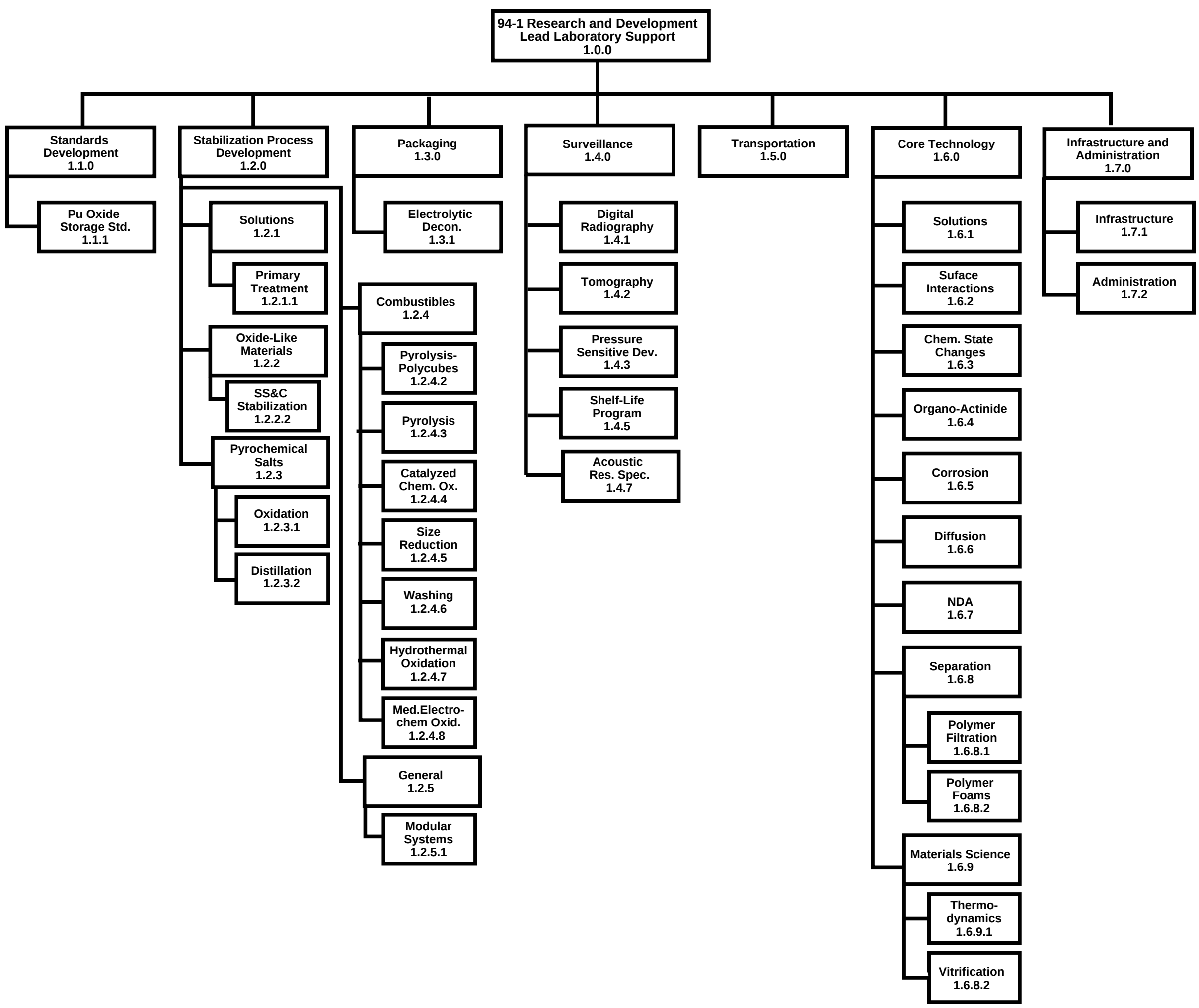

Fig. 1. Work Breakdown Structure.

Work under the Plutonium Oxide Standards Development Project is reported under the Surveillance Metal, Oxide, and Residue Shelf-Life Project.

Sand, Slag and Crucible: High-Gradient Magnetic Separation
Principal Investigator: Laura Worl
Investigator: Coyne Prenger

Task Description. Sand, slag, and crucible (SS&C) residues can have as much as 10%–20% plutonium content. Westinghouse Hanford Company (WHC) has 4300 kg of SS&C residues targeted for treatment and disposal by dry processing. Magnetic separation is a physical separation process that exploits differences in magnetic susceptibility. Almost all actinide compounds are paramagnetic and in a nonuniform magnetic field move in the direction in which the field intensity increases. Diamagnetic particles, such as CaF_2 or MgO, move in the opposite direction. No additional waste is generated. The actinides are concentrated to form a low-volume, actinide-rich stream for subsequent processing and a high-volume, actinide-lean stream.

Status/Accomplishments. We performed experiments on a Los Alamos SS&C residue that was designated MAG26. A particle size distribution of the sample was available. All experiments began with a scalping pass at high belt speed in order to remove any magnetic mineral present. In most cases, this pass resulted in an approximately equal mass split of the feed material. In subsequent passes on the plutonium-contaminated lean stream, we focused on separating the plutonium from the nonmagnetic component. Generally, this can be accomplished at low belt speeds because the plutonium can be influenced by the magnetic body force.

The wide spatial distribution of material exiting the magnetic roll is referred to as “the fan.” The region at the head of the fan usually contains larger diamagnetic particles, while paramagnetic smaller particles populate the region behind the fan. Because the plutonium has a significantly higher density than the SS&C material, the plutonium is influenced by centrifugal forces that act counter to the magnetic force. The result is that the plutonium particles will report to the nonmagnetic fraction, if the belt speed is too high. We attempted to compensate for this movement by varying the location of the splitter bar on the separator. The splitter bar establishes the material collection within the fan.

Figure 2 shows results from the initial processing of MAG26. The scalping pass produced significant concentration of the residue to more than 25 g/kg of plutonium. In the second stage, further concentration occurred to 35 g/kg plutonium. The lean stream concentration was reduced to less than 7 g/kg plutonium. The results suggest that further belt-speed reduction should improve the separation.

The effect of splitter-bar adjustment on the MAG26 results is shown in Fig. 3. An improvement was made in the clean stream, in which we achieved a concentration of less than 6 g/kg plutonium. We made additional runs on the MAG26 sample to determine the influence of capturing the magnetic and nonmagnetic tails on plutonium concentration and to determine whether high grading the rich stream is feasible. We found that variations in the capture of magnetic and nonmagnetic tails were not significant, but that high grading at low belt speeds is a promising technique.

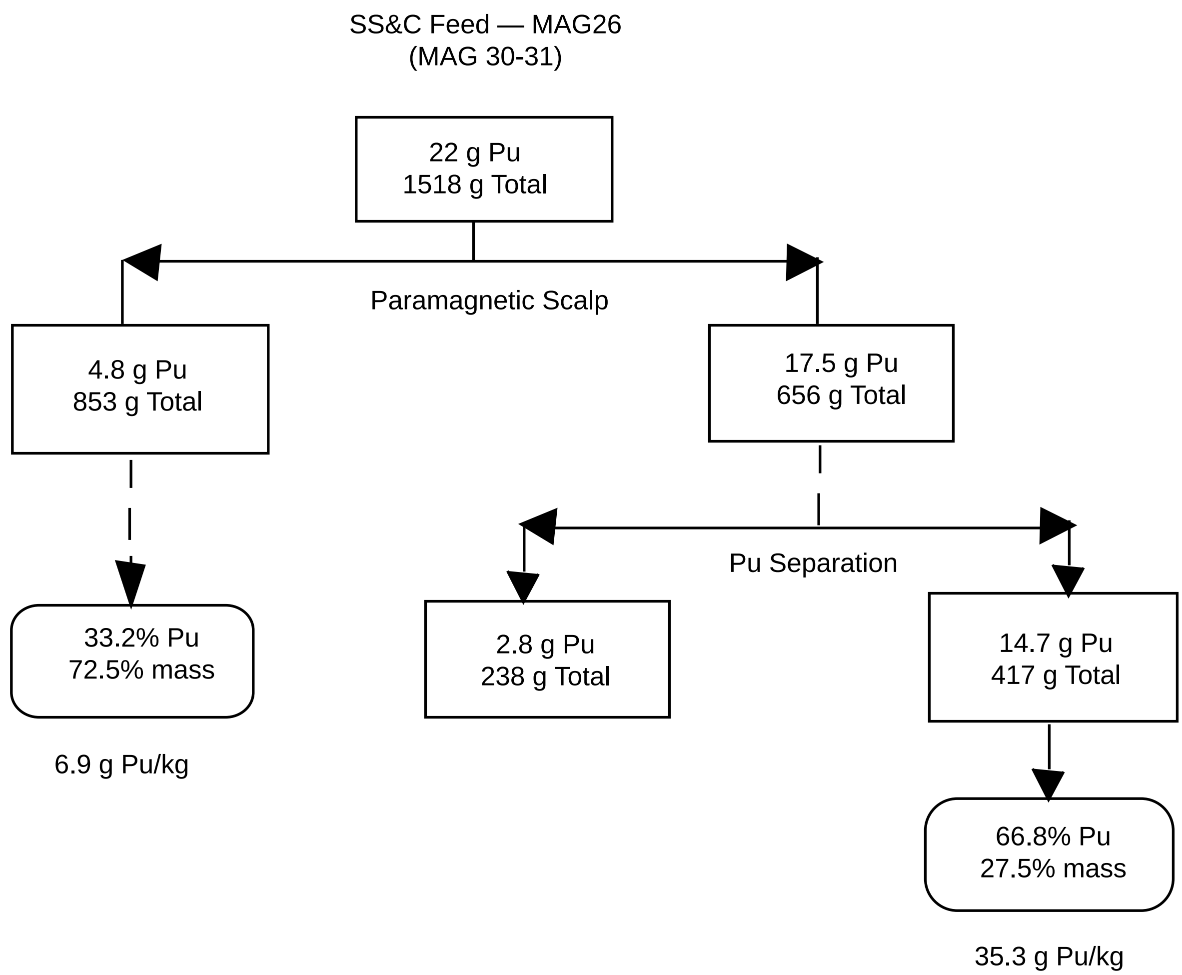

Fig. 2. Initial results of Magnetic Roll Separation on MAG26 residue.

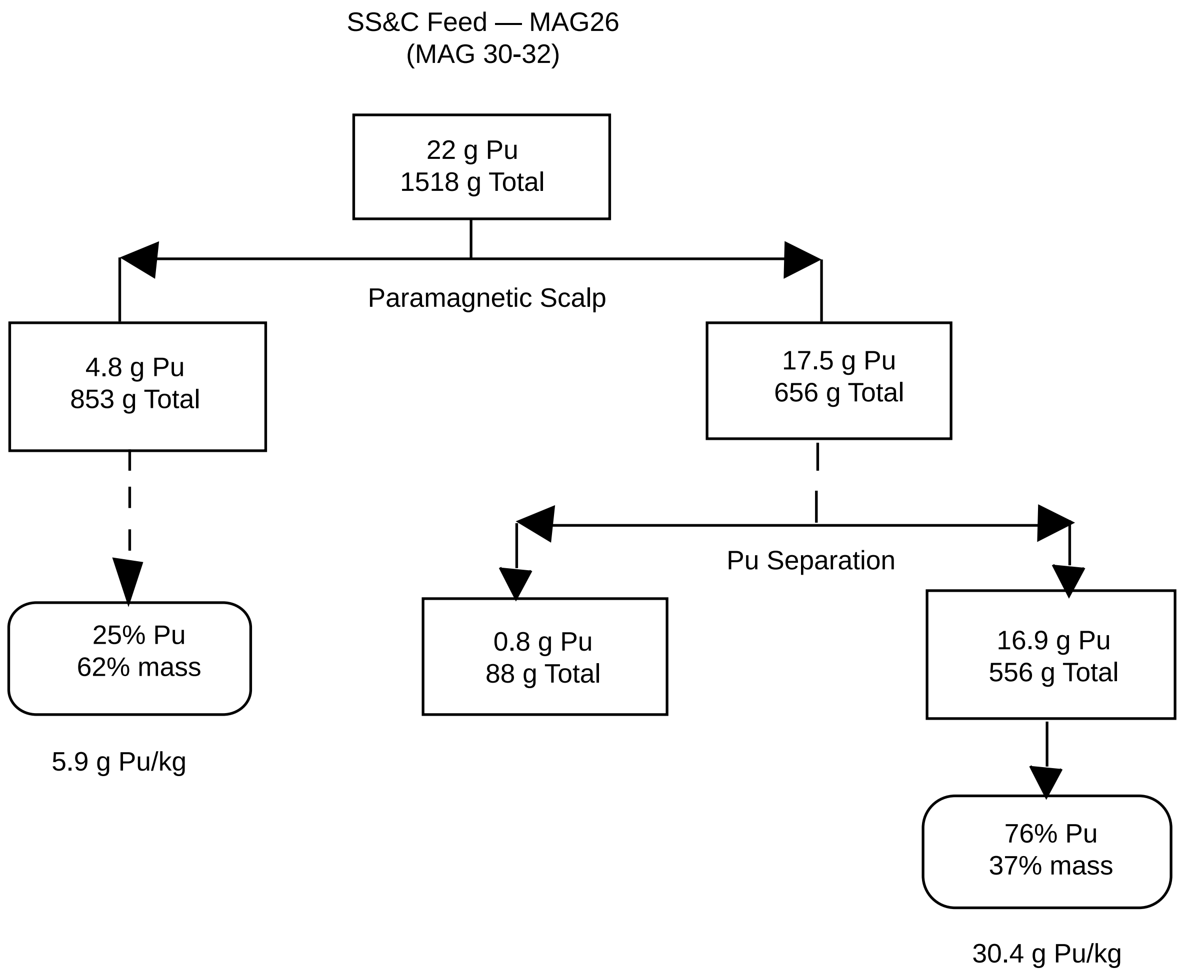

Fig. 3. Results of Magnetic Roll Separation on MAG26 with optimum splitter bar position.

Sand, Slag and Crucible: Cementation
Principal Investigator: Gerald Veazey

Task Description. The objective of the cementation project is to demonstrate and to develop, if necessary, a cementation-based technique to immobilize sand, slag, and crucible (SS&C) waste.

Status/Accomplishments. We did a literature search to look for potential problems with the cementation of SS&C. The only problem we uncovered was a possible delayed expansion effect caused by the presence of MgO, which is a major component of SS&C. The problem stems from delayed hydration of MgO after hardening of the cement, resulting in expansion that causes cracking and pop-outs. We did a set of three scoping tests with Portland type-I/II cement in order to investigate potential expansion problems and to establish the limit for waste loading. We prepared the samples without pH adjustment. We cast the mixes into 2-in. cubes for strength determination according to the American Society for Testing and Materials standard, ASTM C109-92. Other conditions and compressive strength results appear in Table 1.

We considered sample number 1 to have exceeded the limit for waste loading, because the mixer was not able to maintain an adequate vortex or to keep all of the MgO suspended. We experienced no problems in these areas with samples 2 and 3.

We did not perform the 28-day compressive strength test on sample 1, because we wanted to observe that sample for expansion. At the end of the third quarter, we had observed no visible expansion in this sample. An ASTM test exists (ASTM C151-68) for determining the susceptibility of a cemented waste to delayed hydration. This test calls for speeding up hydration in an autoclave and will be performed in order to resolve this issue. Actually, if the expansion occurs, it should not be a problem, because the Waste Isolation Pilot Plant has no restrictions on compressive strength or on particulates. The only concern may be a lessening of the leaching resistance in the total concentrate leachate procedure.

Cementation has several advantages such as low cost for equipment and raw materials, well-established off-the-shelf technology for short implementation time, and ability to adapt the cement formulation to deal with troublesome wastes. SS&C is a good candidate for cementation. The crucible component of the SS&C should serve as an aggregate to improve structural integrity of the cemented waste form. Eliminating the need to perform a pH adjustment will further reduce the complexity of the cementation process.

Table 1. Conditions and Comprehensive Strength Results

Sample	Portland Cement (g)	MgO Crystals (g)	Water (g)	Waste Loading (wt %)	Compressive Strength (psi)		
					7-day	14-day	28-day
1	722	2368	903	59	312	925	–
2	900	1000	900	36	1050	1212	1900
3	900	1500	900	45	1250	1788	2000

Pyrochemical Salts: Salt Oxidation
Principal Investigator: James McNeese

Task Description. Researchers on this project will develop chemical oxidation of spent pyrochemical salts to mitigate safety concerns for interim on-site storage and to optimize the oxidation process to prepare feed for the salt-distillation process. We will perform parametric studies to minimize the amount of oxidant needed to ensure that the oxide heel from the distillation process has the maximum special nuclear material concentration and that the distilled salt has the minimum amount of actinide. Upon completion of process development, Rocky Flats Environmental Technology Site (RFETS) personnel will work at Los Alamos to accomplish the process transfer.

RFETS has 16 metric tons of salt residues that contain 1 metric ton of plutonium. Current plans are to package the processed materials in Waste Isolation Pilot Plant drums. Batches will contain 167 g of plutonium in the unspecified salt content.

Status/Accomplishments. We completed the parameter development for oxidation of salt-strip salts by June 1, 1996. A small dose of sodium carbonate is added to the salts based on the net weight of the salt being processed, as well as on the amount of plutonium contained in the salt. We determined the effectiveness of treatment by making hydrogen-evolution measurements of treated salts in water before and after treatment.

We have begun investigations into the crucible oxidation portion of the project. We designed and tested a vessel on crucibles in sodium chloride/potassium chloride salts. The crucibles were placed into a molten salt; and the mixture was agitated by hand in order to simulate the process in the glovebox. After washing the crucible vessels, we raised them out of the melt and drained the salt away, leaving only a small amount of salt adhering. After the scoping run, we made design modifications on the vessel that will allow for its introduction into the glovebox and for actual process experiments in the process area.

We wrote an experimental plan for plutonium experiments that are scheduled for July and August. Safety facility engineers are now reviewing the plan. We will begin optimizing the process through distillation after the distillation equipment has been installed and tested in its glovebox. This experimentation is scheduled for August 1996.

Pyrochemical Salts: Salt Distillation
Principal Investigator: Eduardo Garcia

Task Description. We will obtain, assemble, test, and demonstrate equipment designed to carry out the salt-distillation process. This process is designed to separate plutonium pyrochemical salts into a very lean fraction (<100 ppm plutonium) and plutonium oxide. The chloride matrix of the pyrochemical residues is converted into totally stable, slightly contaminated salt; and the plutonium is converted into a homogeneous, well-characterized, oxide material that is suitable for long-term storage under DOE standard 3013.

Status/Accomplishments. We had planned to introduce the salt-distillation equipment into a glovebox in late April. However, we had another delay, and we will now place the equipment into the glovebox in mid-July 1996. The following factors caused the delay:

- obtaining facility support for modifications to the glovebox took longer than expected, and
- the number of tests with non-radioactive materials that had to be performed were much more extensive than we had foreseen.

Initial testing with uncontaminated salts is now complete, and glovebox modifications are nearly complete. We will disassemble the equipment during the week of July 1 in preparation for its introduction into the glovebox the week of July 8.

We have made almost 30 test runs with the equipment, using 56 kg of salt. Some minor modifications have been necessary; but, in general, we have demonstrated the ease of operation and have verified design capabilities. We have extensively monitored equipment temperature and pressure during processing. Results and progress for a typical run are plotted in Fig. 4.

The process begins with evacuating the distillation equipment and heating several independent heat zones on the evaporator side of the unit. These zones include the evaporator chamber top, sides, and bottom. A base that holds the salt-containing crucible extends through the bottom of the evaporator chamber, and this base is heated also. In addition, the spool connecting the evaporator and condenser chambers is heated in order to prevent condensation between the two chambers.

As can be seen in Fig. 4, the temperature of the condenser zone also begins to rise. This temperature rise is initially caused by heat conduction on the evaporator side through the metal walls of the unit. When no salt is present in the equipment, the temperature of the condenser stabilizes at ~300°C after ~3 h. With salt present, the temperature of the condenser zone begins to rise faster after ~80 min and increases to ~600°C. We attribute this increased temperature rise to the enthalpy of vaporization from the condensing salt.

Once the evaporation step is finished, the temperature of the condenser shows a drop that is easily observed. Typically, completion of the evaporation step occurs ~4 h after the power is first applied to the furnaces, and an additional hour is usually allocated in order to ensure complete evaporation. At this point, the unit is backfilled with argon to atmospheric pressure; and the temperature of the condenser is raised to 850°C, thereby melting the condensed salt into the receiving mold. The mold itself is heated to 400°C, as measured near the bottom. Molten salt cast into the mold raises the temperature of the side to above 600°C. The melting point of equimolar NaCl-KCl is ~650°C.

After reaching a maximum, the temperature of the mold side begins to fall; and, at this point, the run is considered to be completed. All furnace elements are turned off and the unit is left to cool overnight.

Salts processed in this manner have been easily retrieved from the tapered receiving mold, usually by simply inverting the container, or by gently tapping the mold on a hard surface. The salts have been well-coalesced monoliths that are convenient for disposal. Monitoring the temperature drop in the condenser chamber has served well in signaling completion of the evaporation step, and no salt has been found in the crucible.

Tests runs in the glovebox with clean NaCl-KCl salts are now scheduled to begin by late July. We plan to begin tests with plutonium- containing salts by early-to-mid-August 1996.

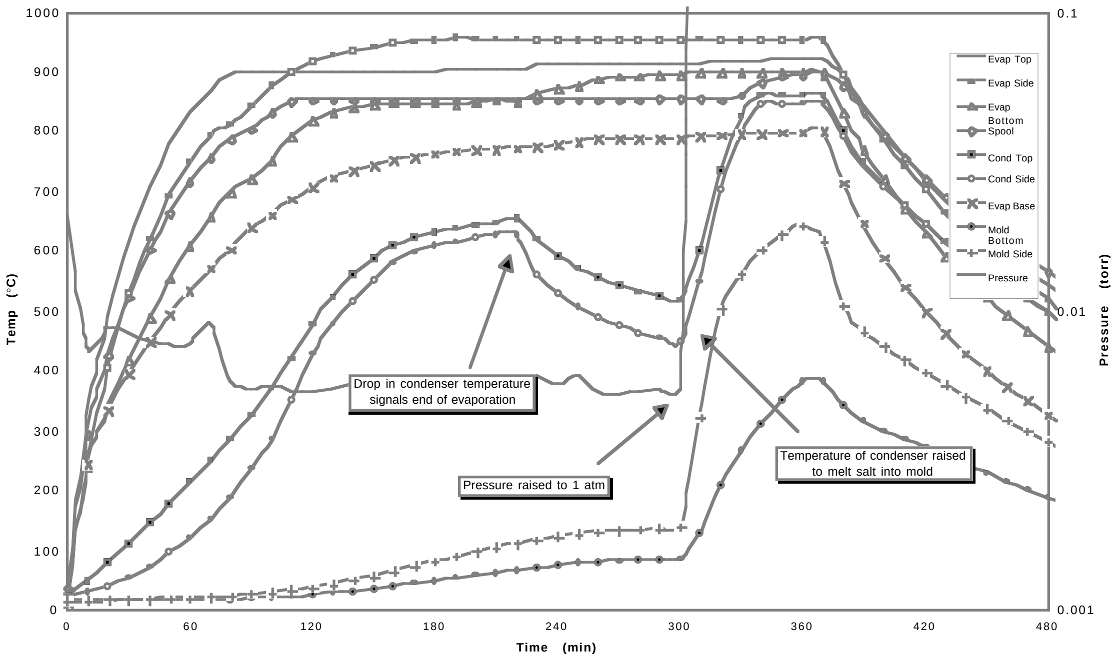

Fig. 4. Results from monitoring temperature and pressure during a typical salt distillation run with 3 kg of uncontaminated NaCl-KCl salt.

Combustibles: Pyrolysis—Polycubes
Principal Investigator: Daniel J. Kathios

Task Description. To perform criticality studies, personnel at various sites in the nuclear complex manufactured plutonium and uranium oxides cast in a polystyrene matrix. Approximately 1600 cubes in storage at Westinghouse Hanford Company (WHC) now represent a waste that is not suitable for long-term storage. Pyrolysis is a pyrochemical technique whereby a high-temperature inert environment is used to break down and volatilize polymeric materials. The aim of this work is to design, test, and implement a pyrolysis system that will effectively destroy and remove the polystyrene matrix, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage.

Tests with nonradioactive materials have shown that the Los Alamos National Laboratory pyrolysis reactor design allows for almost 100% removal of the polystyrene without the formation of tars or other constituents that could adversely affect reactor operation. An off-gas treatment technology must now be introduced that will allow pyrolysis to operate in compliance with environmental and safety regulations and that is suitable for glovebox operations. The pyrolysis system must be delivered to WHC for processing of the remaining inventory of polycubes.

Status/Accomplishments. Los Alamos and WHC personnel reviewed a comprehensive series of design plans for the polycube pyrolysis reactor and the housings for the air preheater and the catalytic converter. This review was to allow WHC to implement modifications that would make the units more compatible for their glovebox operations. Los Alamos personnel made several recommendations, purchased materials, and are now fabricating the units.

We conducted a series of heat-transfer calculations in order to confirm that a metal cooling coil that uses ambient air as the cooling medium could be used to remove the heat required for condensation of the off-gases. In the original pyrolysis setup, we condensed the compounds in the off-gas using a glass-chilled water condenser. Replacing the glass condenser with a metal cooling coil would simplify the operation of the pyrolysis process by eliminating the need for chilled water. Using the metal coil also would improve the margin of safety in the glovebox by eliminating a fragile glass component. We completed the design plans for the cooling coil and are now fabricating a number of these coils.

For complete oxidation of the hydrocarbons present in the off-gas to take place, the air entering the catalytic converter must be preheated before coming in contact with the catalyst. This process is to be achieved by passing the air through a preheater that contains a packed bed of small spherical pellets heated to a high temperature with the 2500-W furnace.

We did a series of mass-balance, energy-balance, heat-transfer, and pressure-drop calculations in order to confirm that the proposed packed bed design would effectively heat the air stream to the temperature required. We also did calculations to determine the type of media that would best achieve this end. The calculations showed that in addition to having a high thermal conductivity for conductive heat transfer, the media must also have an emissivity that comes close to allowing for good radiation heat transfer, particularly at higher temperatures. The results showed that 0.25-in. media, made either of carbon steel or alumina, would be more than adequate for this application. We have purchased a supply of these two media.

We are now conducting tests to confirm the viability of the preheater design and to calibrate its performance as a function of furnace temperature and air-flow rate.

Equipment for the pyrolysis process that is being constructed for WHC must be mounted on a platform that will support the weight of the equipment, allow for convenient and stable plumbing of the process components, and be compatible with a glovebox environment. The platform must be easily shipped, easily disassembled, and easily reassembled in a glovebox. A stainless steel platform was designed using B-Line Strut Systems™. The channel, fittings, nuts, and bolts required to build the system were selected, ordered, and are now being delivered. We compiled a complete inventory of tubing and fittings required to build and test the process; and we purchased the needed materials.

Proper process control and data acquisition must thus be engineered into the system at WHC in order to ensure that the process operates safely and in compliance with environmental regulations. We used a series of potential accident scenarios to identify the proper sensor technology, computer control algorithms, and data-acquisition hardware and software that would be required to maintain safe operation. We reviewed and confirmed the results of this evaluation and gave the data to the Los Alamos Nuclear Materials Technology Division Process Control and Instrumentation Team, who are now identifying, purchasing, and building the hardware and software required for this part of the application.

Combustibles: Catalytic Chemical Oxidation
Principal Investigators: Guy Lussiez and Charles Brown

Task Description. Our objective is to demonstrate catalytic chemical oxidation technology, specifically the DETOX[SM] process patented by Delphi Research, Inc., of Albuquerque, New Mexico. This task includes three major activities:

- design and configuration of the demonstration unit to provide a system ready for glovebox installation in the Los Alamos National Laboratory Plutonium Facility (TA-55),
- continuing development to evaluate final disposition of liquid effluent and spent DETOX reaction solution, and
- installation and testing of the demonstration system on combustible plutonium residues.

Status/Accomplishments. A contract with Delphi is in place to support the design, procurement, and assembly of the demonstration system. We have completed initial process design reviews and have begun process equipment procurement and a glovebox mockup assembly. We identified process utilities requirements. System glovebox modification and installation are scheduled for the first quarter FY97. We began detailed design of the equipment layout within the glovebox. Los Alamos and Delphi personnel completed training on the process control system. An initial design report for the glovebox system is complete, and we have begun work on analyzing accident probabilities and consequences. These reports, combined with previous ones on materials testing and surrogate waste processing, will be used for the process hazards review needed to allow operation within TA-55.

We continued test work on hydrolyzing the DETOX solution and discovered that the reaction progresses along two paths up to about 190°C. At this temperature, the end product is a very hard mixture of ferric oxide (Fe_2O_3) and ferric oxychloride (FeOCl). FeOCI is not very soluble, and it is difficult to wash off. At temperatures around 250°C, when these solids are sprayed with water, FeOCl will form Fe_2O_3. Hydrolysis is about 99% complete, based on the weight of HCl released. Microwave heating makes the whole hydrolysis process faster and easier. To effectively use microwave heating, we need to optimize construction materials. The materials must be transparent to microwaves and must have a very low expansion coefficient in order to resist the thermal shock of water spraying. Spraying techniques must be improved so that water will be evenly distributed on solids. At the scale of the proposed demonstration with radioactive materials, no existing commercial spray is adequate.

Combustibles: Cryogenic Size Reduction
Principal Investigator: Horacio E. Martinez

Task Description. Cryogenic grinding is a process of size-reducing materials at a temperature low enough to keep the material below its glass transition temperature.

Status/Accomplishments. On the filter shredder, we installed safety switches that will not allow the shredder to operate unless the cover is closed. We also fabricated a tray to catch the shredded material. This tray will hold about four filters and can easily have the material it contains emptied into a plastic bag. We opened up the outlet of the cutting-blade housing in order to allow material to more easily pass through. We will test the filter shredder for endurance capabilities.

The Franklin Miller™ low-speed shredder for soft waste has been purchased and will be delivered in about 12 weeks. We have ordered materials with which to test the shredder. We are planning to put the shredder in a glovebox and to interface it with the hydrothermal process. We will visit the vendor on July 18, look at their equipment, and review progress on fabricating the shredder. Testing with nonradioactive materials on the Franklin Miller shredder will begin as soon as it is received. Glovebox modification is also planned. We will run typical soft wastes through the shredder and then perform particle-size analysis.

We have fabricated new cryoblender blades to produce better cutting and liquid control. The original blades produced splashing that would not allow much LN_2 in the blender for cooling. We will test the cryoblender with rubber gloves, Tyvek™, cloth, paper, and plastic sheeting.

The Los Alamos National Laboratory Photo-Video Group will produce a video of the various cryogenic grinding equipment. The video will describe the LN_2 introduction system, the filter shredder, the cryo compactor, and the low-speed shredder. We have reviewed the script for technical content, and filming will begin soon.

Combustibles: Washing
Principal Investigators: Norman C. Schroeder and Moses Attrep

Task Description. Researchers on this project are evaluating the potential application of washing to treat combustible residues, including the advantages and limitations of the technology. Washing does not destroy the organic matrix; but it provides a potentially simple solution to concerns involving hydrogen generation, reactive plutonium metal, and corrosion. We are studying solvent and aqueous washes.

Status/Accomplishments. We mixed oil with residue so that the oil was 28.57% by weight. Cerium was used as a surrogate for plutonium in these studies. Following the flow-sheet plan, we tested batch washing of solvents and cutting oils from the surrogate by washing with CCl_4. This process proved to be an inefficient because of the large hold-up volume of the surrogate material. Because CCl_4 was found to be unacceptable, we dropped the washing step from the base-line feasibility study and focused our efforts on the low-temperature thermal desorption. Scoping studies involving the reactivity of cerium metal with air, steam/air, and boiling water indicated that the oxidation was rather gentle. Below 110°C and under a variety of conditions, the conversion of the cerium metal to the oxide was slow. Complete oxidation of the cerium metal to the oxide was achieved at temperatures between 110° and 150°C.

We conducted a series of experiments on 100 g of wet surrogate that contained CCl_4 and up to 4% cerium metal in a 2-gal. Parr reactor. Quantitative recovery of CCl_4 has been achieved in 1 h. Complete oxidation of the cerium metal is achieved in 1 h if the temperature is maintained at or above 110°C. The oxidation took place in the presence of the cutting oil. The surrogate materials are altered during these processes; this altering of the materials may limit the oxidation conditions to less than 150°C.

Preliminary experiments that use supercritical CO_2 washing method show promise for removing both residual solvent and cutting oil. No further work is planned for supercritical CO_2 processing.

Combustibles: Hydrothermal Oxidation
Principal Investigator: Laura Worl and Steven Buelow

Introduction. The purpose of this task is to design, build, and test a hydrothermal processing (HTP) unit for the destruction of organic and hazardous substances in transuranic contaminated solids and liquids. Oxidation of the organic and reduction of the nitrate components of combustible waste will mitigate safety hazards, reduce waste volume, and facilitate separation of radioactive elements.

Status/Accomplishments. During the third quarter, we completed documentation dealing with safety and engineering concerns. The Los Alamos National Laboratory Plutonium Facility (TA-55) HTP safe operating procedure has been approved. Also during this quarter, we focused efforts on addressing safety concerns related to the TA-55 Facilities Management Group (NMT-8) final Hazards Analysis (HA) and Unreviewed Safety Question (USQ) review. Final HTP work was delayed because it was not listed by TA-55 planners as a priority project. NMT-8 staff assistance to complete the final HA and USQ determination was officially requested by memo, and the request was approved.

The NMT-8 analysis resulted in a list of items to be addressed prior to installation of hydrothermal equipment. Because of these requests, equipment installation was further delayed until July. The major action items that have created the delay are the requests to (1) perform proof testing of all high-pressure components, (2) engineer the pit-burst experiment tie-ins to meet safety concerns, and (3) completely surround the secondary containment with a Lexan™ tertiary containment. We have addressed items (1) and (2), but item (3) remains under discussion. In early June, we considered and finalized action on 18 other requests. Since that time, we conducted testing with nonradioactive materials on the reactor to be installed at TA-55. A Graduate Research Assistant Special Programs guest scientist has recently arrived to work on HTP. He is initially working on testing the reactor with nonradioactive materials.

Our other activities in the third quarter of FY96 included a presentation at the Actinide Separation Conference in Itasca, Illinois, in June. The presentation was entitled, "Hydrothermal Oxidation for the Treatment of Combustibles."

Combustibles: Mediated Electrochemical Oxidation
Principal Investigator: Wayne Smith

Task Description. The purpose of this task is to determine the feasibility of applying mediated electrochemical oxidation (MEO) to the treatment of selected mixed-waste residues. This technology will also be evaluated against alternative treatment technologies to determine which one is best suited for combustibles.

Status/Accomplishments. During the third quarter, we examined the efficiency of destroying spent ion-exchange resins, using cerium(IV) as the electron transfer mediator. Previously, we determined that cerium(IV) may be a better mediator than either silver(II) or cobalt(III), because cerium has much greater stability at the higher temperatures required to completely destroy the resin at a reasonable rate.

Using a pilot-scale reactor and approximately 100-g charges of wet resin, we obtained results shown in Table 2. Results indicate that, under these conditions, resin destruction rate is limited by the chemical reaction between the resin and the mediator, not by the electrochemical generation rate of the mediator. Increasing current density does not proportionally increase reaction rate, and the increase results in overall decrease in current efficiency. In order to increase the reaction rate, either the mediator concentration must be increased or the reaction must be achieved at a higher temperature.

We will perform a few more experiments on the ion-exchange resin/cerium-mediated reaction in order to verify our conclusions and to optimize the reaction rates.

Focus of the work will then be shifted to address the more immediate needs of Rocky Flats Environmental Technology Site (RFETS). This work will involve reconfiguring the MEO system to specifically treat Full-Flo™ filters and high-efficiency particulate air filters that contain contaminated cutting oils and carbon tetrachloride. The goal will be to install a full-scale MEO system at RFETS on the earliest possible date. Equipment design, construction, testing, and chemical-reaction-rate studies will be carried out. We anticipate that we will collaborate with RFETS, Lawrence Livermore National Laboratory, and a private contractor. The contractor will provide a turnkey operation for use at RFETS.

Table 2. Rate of Resin Destruction

Current Density	Temperature	Destruction Rate	Current Efficiency
150 mA/cm^2	60°C	5.8 g/hr	100%
350 mA/cm^2	60°C	6.5 g/hr	55%

General: Modular Systems
Principal Investigator: Richard Hildner and Stanley Zygmunt

Task Description. Researchers on this project will identify tasks within the Rocky Flats Environmental Technology Site (RFETS) Residue Program, in which modular systems may give cost and schedule advantages or in which these systems may reduce uncertainties in the application of the base-line design approach.

Status/Accomplishments. We are developing an integrated and optimized skid-mounted modular system that addresses processing the wet combustibles to meet a residue program commitment for stabilization by October 1998. The wet combustibles trade study should be published in August 1996.

We are developing the design around the two most probable processes. The design would comprise an aqueous system and a pyrolysis or low-temperature thermal desorption unit. The current wet combustible base-line design at RFETS does not separate the plutonium before packaging it for the Waste Isolation Pilot Plant (WIPP). The decision not to separate adds an estimated 20,000 (35% of the total) drums to the WIPP inventory because of the wet-combustible-per-drum plutonium limits. By first separating the plutonium from the wet combustibles to below 0.1%, we can realize significant deposition cost savings and a major reduction of on-site storage requirements for drums at RFETS.

We are also developing an integrated and optimized modular system for unpacking, sorting, and assaying all the backlog residues, then for repackaging and certifying these residues. This scope will address all processing requirements necessary to meet the RFETS commitment to place all residues in a stabilized condition by May 2002. We are developing the design around a skid-mounted system that can be assembled in an existing building at RFETS.

Electrolytic Decontamination Transfer System
Principal Investigator: Timothy O. Nelson

Task Description. Researchers on this project will demonstrate the process for decontamination of long-term storage containers.

Status/Accomplishments. After several iterations, the design of the inner and outer can for nuclear material storage is final. The design is consistent with the British Nuclear Fuels Limited design and with the Los Alamos Plutonium Packaging Project containers. The inner can, 4.5-in. in diam and with 0.060-in. wall thickness, will be fabricated by deep drawing. Specifying emphasis on the product, not the process, we sent a sketch of the proposed can to vendors with expertise in deep drawing and spinning of stainless steel (SS). From the responses, we determined that the can could be deep-drawn to meet our specifications. This process also costs less than spinning.

The can assembly will include one full penetration weld, placed about 1 in. from the top of the can. A Los Alamos quality assurance review determined that the Western Metal Spinning quality management system meets quality requirements; and we ordered 100 containers. We expect delivery the first week of August. Toledo Metal Spinning suggested a deep-drawing and spinning process for the can fabrication. We ordered an additional 50 cans from this company in order to evaluate the process. The outer can will be fabricated from a tube section with two end caps. Current dimensions are for a can that will meet American Society for Testing and Materials pressure-vessel code design for an operating pressure of 500 psi. The can has an outer diameter of 4.92 in. and a wall thickness of 0.118 in. The end caps are 0.354 in. thick.

With can design established, we can complete the design of the fixture for the electrolytic decontamination of material storage cans. The detailed drawings are being generated, and fabrication will begin soon.

We have targeted three process support efforts for electrolytic decontamination of stainless steel, using sodium nitrate solutions: dissolution kinetics, chromium reduction, and filtration of hydroxide precipitates formed in the process. We explored electrodissolution of 304 SS with 38 tests in which the total amount of dissolution was held constant in order to evaluate the effect of operating conditions on surface properties. Variables explored included current density, stirring-rate, nitrate concentration, chromate concentration, and pH. We identified etching, pitting, and electropolishing regimes. We designed and constructed a new electrochemical chromium removal reactor that promises to perform better than the previous reactor did in higher-pH environments.

We completed ultrafiltration tests with the Rhone Poulenc™ membrane system. We began tests with A/T™ Technology membranes made of polymer and observed higher fluxes. Operating conditions that eliminate hydroxide deposition in the 1-mm fibers are being explored. We are developing and evaluating a filtration unit to concentrate and dry the hydroxides. When the precipitate has been continuously removed, higher filtration rates have been demonstrated.

Surveillance: Digital Radiography
Principal Investigator: David Horrell

Task Description. The purpose of this task is to develop real-time/digital radiography for surveillance of stored nuclear materials throughout the DOE complex. Capabilities of the technique will be determined and documented. Hardware and software capabilities will be optimized.

Status/Accomplishments. We are beginning work to characterize the real-time radiography (RTR) system recently installed in the Los Alamos National Laboratory Plutonium Facility (TA-55) by the Plutonium Packaging Project. We are developing initial procedures for inspection and surveillance of long-term storage containers.

At the same time, we will investigate system optimization, with the possibility of system upgrade. The Los Alamos Engineering Science and Application Division's Measurements and Testing Group (ESA-MT) members of our team have completed course work for unescorted access to TA-55 and have almost completed all requirements for access. The ESA-MT team members are working with Savannah River Site (SRS) personnel who have fielded digital radiographic systems. Their experience complements ESA Division experience with digital radiographic and specialty systems. Savannah River personnel visited Los Alamos for initial planning sessions and are scheduled to visit during the week of July 29, 1996, for further system characterization.

The ESA-MT team members have been working with the TA-55 equipment custodian to take measurements of vault storage items. These ESA-MT personnel also performed experiments on ESA-MT radiographic equipment at the Los Alamos radiographic facility. A draft analysis of the real-time system has been generated. Preliminary results show that the system as it is can produce at best an accuracy of ±0.010 in., but it obtains this resolution over a field of view that is only 3.75 in. in diameter. If one looks at a can in a field of view of ≥10 in. in diameter, the resolution is about ±0.030 in. Some ideas for optimizing the current system and upgrading it have been identified.

We propose obtaining film images of all completed Plutonium Packaging Project long-term storage containers. RTR will be performed concurrently, for comparison as a step in the qualification of RTR for long-term packaging surveillance. However, before this comparison can be done, a procedure must be put in place for obtaining repeatable and meaningful data of optimum resolution. It is at this point that the 94-1 R&D Radiographic Development Project and the Plutonium Packaging Project intersect.

A plan has been completed that includes determination of the RTR equipment capabilities and preliminary recording of images for the filled metal cans and bellows, using radiographic film. Following the maximization of machine capabilities and the optimization of parameters, we will take precise bellows measurements on digital media and will record these measurements for future surveillance reference base-line use. We will use statistical support and analysis to update the bellows report (Ref. T. R. Bement, et al, "Analysis of Mini-Flex Prototype Bellows and Initial Production Data," Los Alamos National Laboratory report LA-UR-96-1863 [May 1996]) now to include further testing using the RTR equipment. We will continue recording vault material images and comparing them to actual can-opening occurrences.

Use of RTR images to determine density variations will continue and will be incorporated into the SRS-Los Alamos collaborative efforts. Images of the containers recently received from Westinghouse Hanford Company for shelf-life surveillance studies will play a major role in identifying configurations of those containers to be punctured and sampled for gases, as well as in identifying safety issues in our own vault. Development of digital/real-time radiography and optimization of its use will be shared with other DOE sites, especially Rocky Flats Environmental Technology Site. Hanford has this capability and will share relevant data.

Surveillance: Tomography
Principal Investigator: Lynn Foster

Task Description. The aim of this project is to develop a nondestructive, noninvasive method for determining the contents and the condition of the transuranic materials in containers currently being used. Personnel at Los Alamos National Laboratory and at Savannah River Site will evaluate the feasibility of using computerized tomography (CT) to quantify changes in stored vault items.

Status/Accomplishments. We have designed and constructed the test objects for the computed tomography experimental evaluation. These test objects contain several puck-like objects of tungsten and lead for evaluation of CT imaging of high-density metals and a set of lead compounds for evaluation of dual-energy CT for identification of unknown compounds. We have established a test plan and have contracted with several laboratories and vendors to produce CT data sets from the test objects. Savannah River personnel have generated the memorandum purchase orders specifying the scope of work for the experimental evaluation.

We have already collected an extensive data set to compare the capabilities of the tomographic gamma scanner (TGS) with the current nondestructive assay (NDA) capabilities in the Los Alamos National Laboratory Plutonium Facility. We have collected data for the evaluation using the TGS, neutron coincidence counting, multiplicity neutron counting, conventional segmented gamma scanning, and calorimetric assay. Given the unique opportunity to evaluate the TGS in our facility, we are continuing to collect data to enhance the database and to extend the knowledge base for TGS/NDA operation.

Surveillance: Pressure-Sensitive Devices
Principal Investigator: David Horrell

Task Description. The primary goal of this project is to develop a solid-state sensor to measure hydrogen concentration within the material container, using power deployment and data telemetry systems that do not breach either the outer or the inner container. Phase I of this multiphase effort is a proof-of-concept project for monitoring nuclear materials. We are hoping to have a prototype system delivered to Los Alamos by the end of October 1996, so that laboratory testing can begin.

Status/Accomplishments. We are anticipating the following environmental constraints in connection with the system:

- hydrogen pressures may be less than 1 atmosphere to upwards of 2 atmospheres in hermetically sealed stainless steel containers with plutonium or plutonium oxide stored in them;
- the containers will normally be in vaults with the temperature in the inner container being about 50°C, although it may be possible that the ambient temperature may drop to near 20°C; and
- the total radiation dose rate that the system may be exposed to is approximately 0.5 rads(si)/h, which requires that for a 50-year lifetime, we either use radiation-hard components or shield the system.

We have chosen to shield the system from the radiation because shielding is easy to do when using ~1 mm of tantalum or tungsten and also because the cost saving is a factor of 100 when using commercial parts over radiation-hardened ones. Preserving the integrity of the container also put a constraint on the amount of power that can be coupled into the inner container to electrically drive the sensor and to extract data.

The Sandia National Laboratories, New Mexico, hydrogen sensor itself consists of the following components:

- a hydrogen-sensing transistor for monitoring the subatmospheric range,
- a hydrogen-sensing resistor for the ≥0.5% hydrogen regime,
- a diode for measuring the temperature of the chip and its proximity, and
- on-chip heaters for maintaining on-the-chip constant temperature.

Under a different contract, the basic Sandia hydrogen sensor technology has been commercially licensed, and technology transfer is under way.

Because the amount of power that can be coupled is not enough to power up the heaters, they will not be used. The chip temperature, transistor, and resistor signals will be collected, digitized, and piped out to the data analysis equipment for further analysis.

Sandia researchers have developed models for the diode and resistor that will allow the signals to be temperature-compensated and a clean hydrogen signal to be extracted. The transistor will be operated in a regime where the effect of temperature is minimized. For the first prototype system, hydrogen sensors have been fabricated, packaged, and run through a set of tests in hydrogen ambients in order to allow them to plug into the system.

At Sandia, further characterization is under way in which the hydrogen sensor is tested in a number of hypothetical hydrogen ambients. Other efforts are aimed at fabricating new sensors with different catalytic metal alloys to allow the sensor to withstand much higher hydrogen pressures without going through catalytic metal phase transition; this transition would cause the sensor to self-destruct. Work is under way that will target getting more sensitivity out of the sensor by series connections of more than one sensor element.

The power and telemetry system are combined and basically involve supplying power through the two stainless steel containers, powering up the hydrogen sensor, collecting data (temperature and hydrogen pressure), and then extracting the data—all without breaching the container. In June, Los Alamos project team members witnessed the transmission of a signal across a double wall, thus demonstrating that we have developed the telemetry necessary to remove and process the information for hydrogen concentration.

The power transformer circuit is presently being engineered by Sandia. Two implementations are under consideration—one is a core type, and the other is a self-supporting coil. The core type meets the power specifications for the hydrogen pressure sensor and its interfacing circuitry. The self-supporting coil, though, is highly regarded because it is easier to mount in the container than is its core counterpart. The coil is also more shock-resistant than the core. However, the coil has to be tested further in order to determine whether it meets the power requirements for all the components.

Sandia has prototyped the accompanying analog-to-digital (A/D) conversion circuitry. An emulation of the container-coupled power circuit presently powers the prototype. Simulated voltage signals have been successfully used in place of the hydrogen sensor's signals to test the A/D operation. The process of interfacing A/D circuitry to the hydrogen sensor is being tested and implemented. In particular, the voltage circuit for the sensor needs to be built, with consideration being given to the system power specification. Sandia is also presently engineering the data transmission. In the data retrieval, the hydrogen-sensed data needs to pass out through the containers just as the input power does. A transformer circuit with high-frequency characteristics is under design by Sandia.

A calibrated device for use within a plutonium oxide container system will be ready for testing at Los Alamos in October 1996.

Surveillance: Metal, Oxide, Residue Shelf-Life Program
Principal Investigator: David Horrell

Task Description. The goal of this project it to evaluate the behavior of plutonium metal, as well as pure and impure oxide, in storage and to evaluate the compatibility of these materials with their containers.

Status/Accomplishments. The Los Alamos National Laboratory Nuclear Materials Technology Division's Weapons Technology Group (NMT-5) has hired a technician to support the project. Material prepared by the oxide processing personnel in the Nitrate Systems Group (NMT-2) will be characterized and loaded into surveillance containers, on which pressure-volume-temperature data will be gathered, as well as thermal desorption measurements of materials and mass spectroscopy of evolved gases. Several items of capital equipment were purchased for NMT-5.

A Materials Identification and Stabilization (MIS) working group has been established including representatives from each of the sites holding legacy materials to be stored long-term. A meeting of this group was held at the Rocky Flats Environmental Technology Site (RFETS) in June, with representatives from Westinghouse Savannah River Company (WSRC), Westinghouse Hanford Company (WHC), RFETS, and Los Alamos participating. A path forward was established, and a trip report was issued. A weekly MIS conference call to discuss issues and update sites has been initiated. In addition, the MIS working group will meet regularly at different sites.

The following major developments have occurred in the third quarter:

- the agreement by the Los Alamos National Laboratory Chemical Science and Technology TA-55 Materials Characterization / Analytical Chemistry Group (CST-15) to support analysis of surveillance materials and
- the decision by WHC to ship items of interest to Los Alamos for surveillance studies.

With the support of CST-15, project researchers can make large strides toward accomplishing our goals and tasks of evaluating untreated and stabilized legacy plutonium materials. A preliminary report on the history and capabilities of loss-on-ignition (LOI) analysis has been completed by CST-15 personnel. CST Division can support x-ray, LOI, thermal desorption, mass spectroscopy, surface analysis, and chemical analysis.

Analysis personnel from CST-15 attended the June MIS meeting at RFETS to learn the needs and indicate support of the overall effort. RFETS is our biggest customer, has the greatest need of support, and, consequently, will be the focus of our goals. With the almost total loss of analytical capabilities at RFETS, Los Alamos has been asked by the Safe Sites Of Colorado repackaging group to support their requirements. CST-15 personnel can best accomplish this need and have demonstrated a willingness to do so. The LOI measurements currently completed at RFETS are considered to be meaningless because of the sampling size and subsequent analytical results. Los Alamos is supporting RFETS in order to meet LOI and other requirements.

Materials from RFETS will be shipped to Los Alamos for inclusion in the Shelf-Life Project in FY97. WHC will be shipping materials immediately. Some of the materials shipped from WHC were generated at RFETS and represent current RFETS holdings that are suitable for evaluation. Los Alamos will support RFETS needs to establish a shipping capability.

Hanford personnel have added immeasurable support to the surveillance development program by identifying plutonium legacy materials that have aged in storage for almost 20 years and that include both pure and impure oxides. These materials represent current holdings at several DOE sites and are surrogates for oxides stabilized to a 700°C calcination temperature. Thanks to the support of DOE Albuquerque, WHC materials will gain entry into the Los Alamos surveillance development program during the last quarter of FY96. The MIS working group is currently writing the experimental plan for these materials, with the support of NMT-5, NMT-2, and CST-15. These three Los Alamos groups will carry out the plan. This endeavor includes the gas sampling of all containment in its various configurations. Complete analysis of the plutonium-bearing materials will include LOI, particle-size analysis, chemistry, isotopic assay, and water re-adsorption after calcination at several temperatures. Visual, photographic, and real-time radiographic images will be matched to images taken during opening of materials containers. Results of testing will be made available to participants immediately.

Savannah River Site (SRS) personnel will supply materials for evaluation to determine the utility of thermal stabilization on mixed oxides and alloys. After the SRS F-Canyon is closed, thermal stabilization will be the only SRS avenue for DOE-STD-3013-94 preparation for long-term storage.

Los Alamos personnel have completed characterization of the first impure oxide including the chemical analysis and will distribute a report in July. The material from the Los Alamos inventory to enter the program will be a plutonium-uranium mixed oxide.

In the investigations of optical monitoring techniques, Los Alamos researchers have just completed fabrication of storage cans for the studies. We are now able to begin experiments in Building PF-42 of the Los Alamos National Laboratory Plutonium Facility (TA-55), using laser-induced breakdown spectroscopy (LIBS) system to evaluate different gas compositions introduced into the cans. This ability to run experiments will allow us to optimize the detection of changes in the gas composition and the detection of the amounts of gas.

We continued experiments on gadolinium, using the experimental setup detailed in the second quarter's report. The start-up of experiments on plutonium oxide powders and plutonium residues in TA-55, Building PF-4, is still awaiting relocation/modification of the Advanced Recovery and Integrated Extraction System (ARIES) gloveboxes.

Surveillance: Acoustic Resonance Spectroscopy
Principal Investigators: Kirk Veirs and Clinton Heiple

Task Description. We are studying acoustic resonance spectroscopy as a method to noninvasively monitor gas pressure and composition in storage cylinders containing plutonium-bearing materials.

Status/Accomplishments. With a minor modification to the container, we conducted initial experiments that demonstrated the feasibility of simultaneous pressure and composition measurements in filled storage containers at pressures comparable to those expected in actual use. We have now demonstrated in a simulation of double-containment storage geometry that gas resonances can be created and observed in the inner can with transducers mounted on the outside of the outer can, using mechanical coupling between the two containers. We tested several coupling geometries, including stainless steel cylinders that were 0.25 in. in diam × 0.25 in. high, 45° stainless steel cones that were 0.25 in. high, and a stainless steel thin-walled ring that was 0.25 in. high. The cylinders were the most effective. Epoxying the cylinders in place produced the best signal. The signal was much reduced when epoxy was not used and the cylinders were held to the two walls by clamping the two plates together.

The initial modification to the inner can involved creation of a 1-in.-thick analysis chamber in which the gas resonances were excited. Because such a chamber uses an appreciable fraction of the space available for residue storage in the container, we evaluated thinner simulated chambers. Satisfactory signals were obtained with a 0.25-in.-thick chamber, and detectable signals were obtained with chambers as thin as 0.106 in.

Many container-shell resonances are within the frequency ranges in which gas resonances are expected. These shell resonances can interact with the gas resonances and are likely to be a significant problem in analyzing signals from actual material-filled storage containers. We are creating an alternate design for the analysis chamber. We expect that in this configuration, the residue will damp many or most shell resonances, thereby improving our ability to detect and measure gas resonances in the analysis chamber. We expect to begin testing shortly.

Interaction between gas and shell resonances is a substantial problem in signal analysis. As the driving frequency approaches a shell resonance, the amplitude of shell wall motion increases. If this motion can be coupled to gas motion, the gas will be driven harder, leading to a larger gas peak signal. Transfer of energy to the gas extracts energy from shell motion and reduces its amplitude. We tested this physical model numerically by calculating the signal amplitude as opposed to frequency resulting from the sum of two damped, driven harmonic oscillators interacting as described. The similarity between calculated results and experimental observation suggests that the physical model of the interaction is substantially correct.

Core Technology: Actinide Solution Chemistry
Principal Investigator: John M. Berg

Task Description. The goal of this work is to describe aspects of the solution chemistry of actinide elements in legacy residues and in proposed residue treatment processes. The purpose of such description is to guide stabilization and disposition decisions and to enable efficient optimization of treatment processes.

Plutonium residue stabilization and treatment processes must be efficient and must be targeted at the present-day issues of safety, stability, and economics of disposal. Aqueous chemical separations will be required for primary treatment and post-treatment following stabilization of many of the residues. These aqueous separations must be carried out under chemical conditions that differ considerably from those used in production of materials for weapons. We propose to measure critical thermodynamic parameters governing actinide chemistry under these chemical conditions, so that treatment and separation processes can be designed and optimized quickly.

Status/Accomplishments. Plutonium solution data acquisition activities are continuing at a high level for both nitrate and combustible process effluents. Plutonium nitrate data acquisition overall progressed less than expected during the third quarter because of ongoing service connections being made to our gloveboxes, room reconfiguration activities for the Advanced Recovery and Integrated Extraction System (ARIES) Project, and the annual special nuclear materials inventory. Only the last interruption was anticipated. All were largely out of our control. Data analysis began during the third quarter, but it will not be fully completed until late August because that activity depends on the data acquisition as input. However, we can draw interim technical conclusions.

Since resuming experiments in mid-June, we have taken spectra of an additional 100 solution samples to further map out the plutonium nitrate system. We upgraded our capabilities by adding a flow cell and pump to the spectroscopic apparatus, allowing us to reduce sample preparation time, sample handling, sample volume, and waste generation, while improving the reproducibility of the spectra. Overall, since it was implemented in mid-June, this improvement has increased our weekly data production by about a factor of two.

We have completed initial data analysis on spectra taken through the end of March. We found that high-electrolyte concentration alone has a significant effect on the spectra or plutonium species in these solutions and that the effect is different from that of complexation by nitrate. This information will have to be taken into account in further analyses. We have initiated a collaboration with the Los Alamos National Laboratory Chemical Science and Technology Nuclear and Radiochemistry Group to evaluate different methods of modeling the background electrolyte effects.

We are focusing our combustible process effluent studies on acquiring data about the plutonium carbonate system and the competing effects of chloride. These studies began during the third quarter of FY96, are progressing smoothly, and are on schedule in the Los Alamos Chemistry and Metallurgy Research Building.

Core Technology: Chemical and Physical Interactions of Actinides with Surfaces
Principal Investigator: David Morris

Task Description. Researchers are studying chemical interactions and surface structural characteristics of plutonium and uranium species adsorbed onto solid-phase materials found in processing residues throughout the DOE complex. The information provides a basic framework of surface interactions that can be incorporated into future stabilization activities.

Status/Accomplishments. We initiated new research activities in a number of areas and are making advances in scoping experiments. In addition, we are sponsoring an undergraduate research student under the auspices of the Los Alamos/Furman University Students Program and are also moving forward on post-doctoral recruiting to provide support for the imaging microscopy effort. We have identified six postdoctoral candidates and have contacted them for additional information.

We successfully demonstrated that our instruments can generate a spatially resolved Raman spectroscopy map and a wider-area x-ray-fluorescence elemental map of a surrogate heterogeneous uranium sample. This information is important for applying imaging Raman spectroscopy to speciation studies of actinide-containing ash samples and other residue materials that contain heterogeneously dispersed plutonium.

We began a resonance Raman and luminescence study of ion-exchange resins as a function of accelerated aging and stability in the presence of concentrated nitric acid. We are studying both anion (Dowex 11™) and cation (Dowex 50™) resins. Both resins were found to luminesce strongly in the visible region. We observed vibrational bands for nitrate and for the resin backbone modes. We detected no significant resin degradation (based on Raman signatures) after two weeks of aging at ~50°C.

Before we studied the surface interactions of nitrato-complexes of uranium and plutonium with anion-exchange resins, we did luminescence spectroscopic studies of the solution nitrate-complexation of U(VI). Our studies are in the range of 0–12 M nitrate at variable acid concentrations. We are observing interesting luminescence-quenching behavior in conjunction with the transition from aquo complexes to nitrato complexes.

Construction is progressing on the new laser spectroscopy facility for actinide residue characterization studies. The Fourier transform infrared microscope is now operational. The red Raman microscope system components are being installed and will be tested during the fourth quarter of FY96.

Core Technology: Changes in the Chemical State of Plutonium
Principal Investigator: Kirk Veirs

Task Description. The purpose of this work is to identify and characterize changes in the physiochemical state of plutonium compounds found in residues using x-ray diffraction, x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy, and optical spectroscopies.

Status/Accomplishments. We conducted the first XAS spectroscopy run at the Stanford Synchrotron Radiation Laboratory under 94-1 R&D funding March 28–April 8, 1996, collecting data on three series of plutonium-containing samples.

The first series of samples was plutonium in the +3, +4, +5, and +6 oxidation states in solution and complexed with water. No other complexing species were present. We will use this series to establish the sensitivity of x-ray absorption near-edge structure (XANES) spectroscopy to the plutonium oxidation state.

A second series of samples consisted of plutonium hexanitrato species that were absorbed onto anion-exchange resins in which the resin-active site was chemically modified. We will use this series to elucidate the effect of exchange-site geometry and charge on the structure of the absorbed plutonium species.

The third series of samples consisted of plutonium oxide in which the amount of oxygen was varied to produce a range of oxygen concentrations from substoichiometric to superstoichiometric. We will use this series to examine the structure of plutonium oxides and to evaluate the capability of XANES to obtain average oxidation states for oxides.

XANES spectroscopy is an established technique for the determination of oxidation state and local chemical environment, even in relatively dilute solutions. XANES studies could also furnish oxidation state information at the solution/surface interface in sorption experiments and solid precipitate information from environmental samples, provided that the edge energies and characteristic absorption spectra are well understood. While XANES spectra from the complete suite of neptunium oxidation states have been reported, no reports on systematic XANES studies of an oxidation-state series for plutonium complexes have been made. In this work, we demonstrate the efficacy of XANES spectroscopy for plutonium speciation studies.

Besides using the first zero crossing of the second derivative as the edge energy, we also fit the XANES spectra to a linear combination of an arctan and two Gaussian functions, in which the arctan is meant to fit the $2p^{3/2} \rightarrow$ continuum transition ("edge") and the lowest energy Gaussians to fit the bound $2p^{3/2} \rightarrow 6d$ transition ("white line"). This type of fit has been used because it has been typical of those for other actinide reports, especially for uranium and neptunium. Also, use of this fit avoids interference from the "white line," when determining the XANES edge. However, the identification of the "white line" signal versus early extended x-ray absorption fine structure (EXAFS) signal remains unclear and detailed modeling is in progress. In this work, we concentrate on whether XANES can be used empirically to determine plutonium oxidation states.

From our data on aquo ions of plutonium in oxidation states (III), (IV), (V), and (VI), we see a clear difference between the general spectral shape of the III and IV species versus the V and VI species that contain "yl." Specifically, the "white line" is considerably sharper in the spectra of the former pair. We have seen this feature in uranyl compounds [U(IV) in contrast to U(VI) species] as well.

The energy in the edge and "white line" positions is listed in Table 3. When we measured the edge shifts by the second derivatives, we found that they generally increase with the formal oxidation state of the absorbing metal atom; but we note that the edge energies alone cannot distinguish between Pu(IV) and Pu(V). However, when fit to an arctan and two Gaussians, the edge (arctan) energies do increase progressively with the oxidation states; and we find an excellent linear correlation between the edge position and plutonium oxidation state (r2 = 0.997). Addition of a third Gaussian to the XANES deconvolution for the V and VI species affected the edge position only marginally (Table 3), and we still conclude that higher edge position correlates with oxidation state.

Table 3. XANES Data for Plutonium Complexes*

Sample	Second Derivative	Arctan	Gaussians First	Gaussians Second	Gaussians Third
Pu^{3+} aquo	18059.6	18055.8+0.6	18062.8	18069.5	
Pu^{4+} aquo	18062.7	18057.6+0.4	18067.4	18075.8	
PuO_2^{+} aquo	18062.1	18059.4+0.3	18065.5	18071.6	
PuO_2^{+} aquo	18062.1	18060.2+0.4	18065.7	18072.1	18099.8
PuO_2^{2+} aquo	18064.5	18060.8+0.2	18067.9	18075.2	
PuO_2^{2+} aquo	18064.5	18062.0+0.6	18067.9	18074.6	18104.9

*All data are in eV.

An increase in formal oxidation state implies an increase in effective charge, and it has been shown that x-ray absorption-edge energies are governed mainly by the effective charge on the absorbing ion or atom. More specifically, the effect of different oxidation states stems predominately from Coulomb attraction between the core hole and the 5f electrons in the actinide. This attraction in turn depends on f-orbital occupancy and on localization. From this work, it seems clear that XANES spectroscopy can be a useful tool in plutonium oxidation-state studies, both from the spectral features (III and IV in contrast to V and VI) and from the arctan-edge energy.

Preliminary analysis for the data collected on the resin samples suggested differences in the extended EXAFS that may be correlated to molecular structure. This finding is very encouraging, because the major differences are thought to exist at the binding site for the $Pu(NO_3)_6^{2-}$ species on the resin, and these differences would involve the atomic shell that is fourth away in distance from the central plutonium atom. The EXAFS would be expected to be weak for this shell. We are doing additional data analysis, including analysis of data from plutonium-containing incinerator ash that was also collected during the April XAS run. We ordered and recently received a new computer that is capable of running the necessary software under the Open Virtual Memory System (VMS)™ operating system. The Los Alamos National Laboratory Nuclear Materials Technology Division Weapons Component Technology Group provided the oxide samples.

Core Technology: Actinide-Organic Interactions
Principal Investigators: Carol Burns, Steven McKee, and Ann Schake

Task Description. Researchers are exploring interaction of plutonium and other actinides with organic substrates. We will study interactions between actinide residues and organic substrates (chemical speciation) and actinide organometallic chemistry (organo-actinide chemistry). We began in third quarter of FY96.

Status/Accomplishments. The project is on schedule for selecting residues for combustible technology demonstrations and readiness review requirements. We delayed hiring a postdoctoral fellow, but sufficient personnel are currently available to conduct the project.

By August, we will prepare an experimental plan that includes task description, deliverables, and milestones. Representative organic materials that we propose to investigate include plastics (polystyrene, kynar, and polyethylene / polypropylene), flow-through filters, high-efficiency particulate air filters, and butyl rubber gloves. We will study surface characterization of actinides entrained on these organic materials. We will prepare samples and will simultaneously obtain, for comparison, actual plutonium-bearing samples from Los Alamos National Laboratory inventory. Aqueous experiments will begin August 1 of FY96.

As the matrix destruction caused by oxidation of the organic matrix proceeds ultimately to CO_2 and H_2O, these organic materials will be broken down into monomer / oligomer units, with an organic intermediate carboxylic acid / carboxylate species. We are preparing several representative carboxylic acid compounds in order to explore speciation of carboxylic acids with aqueous plutonium. For the initial experiments, the plutonium species will be Pu(IV) nitrate and Pu(IV) chloride. Another system of interest regarding organic speciation is the decomposition of tributylphosphate (TBP) in the presence of plutonium. Some of the TBP intermediates readily bind with plutonium. We will study speciation and decomposition at elevated temperatures and will compare the results with decomposition at room temperature. We will use both nitrate and chloride media.

All appropriate requirements concerning environment, safety, health, facility, and accountability are in place. By August, we will update our safe operating procedures. We are preparing Criticality Safety Limit Approval forms. To eliminate a potential safety hazard, we must modify an inert glovebox used for synthesis of actinide precursor materials necessary to the scheduled organo-actinide tasks. We are exploring alternatives, if the glovebox cannot be made ready by August 1.

Core Technology: Corrosion
Principal Investigator: Darryl P. Butt

Task Description. Researchers on this task are studying the effects of crystallographic orientation on the electrochemical behavior of materials. The objective is to correlate the effects of individual grain crystallographic orientation with the localized corrosion behavior of these grains. The purpose of these correlation studies is to discern the effect of surface structure on pitting and to gain insight into the stochastic nature of corrosion.

Status/Accomplishments. Our initial efforts included a thorough literature review, materials selection (beryllium, nickel, titanium, and stainless steel), and preparation of textured materials. Preliminary electrochemical tests have been performed on beryllium and nickel. Initial results from potentiodynamic polarization experiments that incorporate beryllium exposed to chloride environments are promising. We found that pitting is associated with certain individual grains and that the pits are composed of crystallographic facets. For these initial tests, we did not attempt to study correlation between particular orientations and pitting susceptibility.

Ensuing research will begin with orientation imaging microscopy (OIM) to determine the orientation of each individual surface grain, then electrochemical tests to determine the relative susceptibilities of particular orientations. Beryllium samples have been prepared for and are currently awaiting OIM study, which is scheduled for late July.

Additionally, we have performed preliminary electrochemical experiments that incorporate nickel that has been exposed to chloride solutions. The results we have from these tests are not as definitive as those we have on beryllium, and refinement of the experimental procedure is still ongoing.

In addition, we have recently discovered a narrow set of conditions in NaCl-nitric acid environments in which we can get faceted corrosion pits in stainless steel (Fig. 5). We are currently studying to assess the mechanism for this pitting.

Near-future work for this project will include OIM of beryllium samples, electrochemical and OIM testing of nickel and stainless steel samples, and assembly of a scanning reference electrode system for surface mapping of localized corrosion sites.

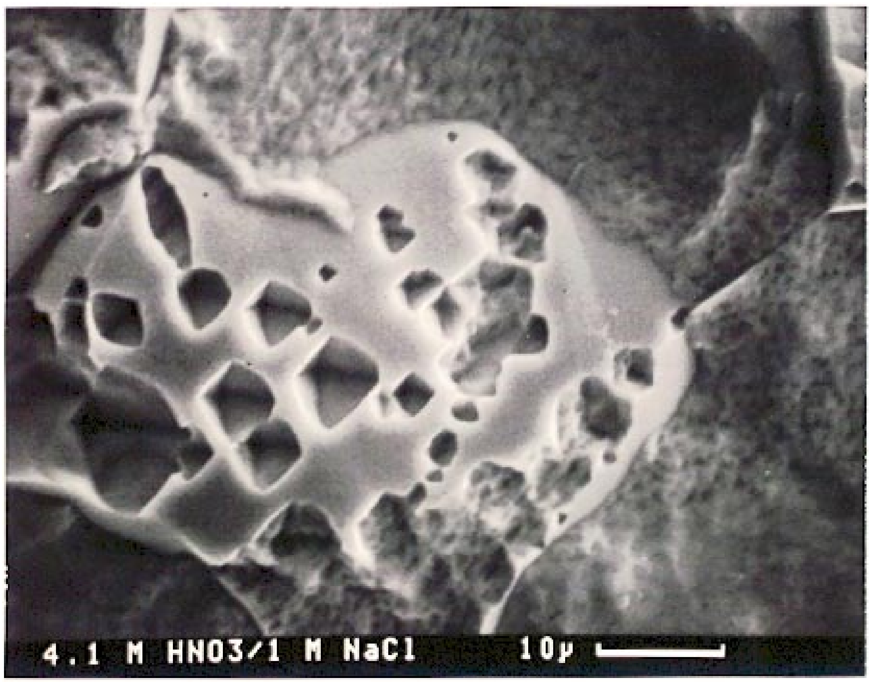

Fig. 5. Corroded surface of 304 stainless steel, showing faceted pits on a single grain.

Core Technology: Plutonium Diffusion Science
Principal Investigator: Pamela K. Benicewicz

Task Description. Researchers on this project are seeking to measure and understand the diffusion of plutonium into materials, such as stainless steel, at room temperature and over long times.

Status/Accomplishments. We held detailed discussions with Los Alamos National Laboratory and Argonne National Laboratory (East or West) personnel who possess various technologies that will aid in determining the diffusion of plutonium into various metal matrices. Members of the Los Alamos Chemical Sciences and Technology (CST) Division can provide the following analyses on samples of metals that have been in contact with plutonium for known periods of time: bulk plutonium analysis using inductively coupled mass spectroscopy, elemental surface maps using x-ray microfluorescence, depth-profiling using time-of-flight secondary mass spectroscopy (TOF SIMS), detection limit determination using Quadrupole SIMS, cross-section depth analysis using scanning electron microscopy (SEM). Argonne-W can provide some high-temperature accelerated-aging treatments of plutonium with uranium and stainless steel and can provide SEM analysis to correlate these high-temperature diffusion results to the Los Alamos room-temperature diffusion results.

As our first materials for this diffusion study, we obtained beryllium metal that had been in close contact with plutonium metal for ~30 years. Samples have been sent to CST for initial analyses, and we are awaiting the results. Other diffusion systems of interest—plutonium into uranium and plutonium into stainless steel—have been identified, and sources of materials have been found. We will be able to obtain samples in July, August, and October.

We have begun experimental work on determining and refining the depth-profiling capabilities of laser ablation spectroscopy. With this technique, surface layers of metal materials that have been exposed to plutonium are removed by laser ablation, while plutonium concentration is determined by spectroscopy. We are investigating how to improve this depth resolution by varying the laser system parameters of laser energy, focal length of the focusing lens, and buffer gas and buffer-gas pressure. We have begun experiments with nonradioactive materials, using stainless steel; and we are in the process of having coatings of known thicknesses deposited on stainless steel in order to determine the depth resolution of our technique.

Core Technology: Nondestructive Assay—Surveillance of Plutonium
Principal Investigator: Teresa Cremers

Task Description. Focus of this work is on the empirical evaluation of neutron generation resulting from transforming plutonium metal into compounds and the resulting alpha-n interaction. We are also looking at determining the isotopic distribution in heterogeneous plutonium-bearing salts.

Status/Accomplishments. In the surveillance of changes in stored plutonium by neutron multiplicity counting, we have completed the measurements outlined in our proposal and have begun analysis of the data. Initial results suggest that the measurements are not as sensitive as we might like. This portion of the project will likely terminate after the data evaluation.

The work on gamma-ray isotopic distribution of heterogeneous plutonium-bearing salts is proceeding on schedule. We have identified the necessary parameter sets to analyze heterogeneous materials; and we are beginning to perfect these sets.

In evaluation of salt-distillation residues, we have examined the gamma-ray and neutron-emission rates, which correspond to our expected detection limits. We have determined that we can meet our needs with a simple gamma-ray detection system. Our work is on schedule, and we expect to have the final report done on time.

Core Technology: Separations—Polymer Filtration
Principal Investigator: Gordon Jarvinen

Task Description. Researchers on this project will remove actinides from solutions to achieve very low levels of concentrations in order to meet liquid discharge requirements. The objective of this task is to optimize the polymer filtration process through understanding key properties of the polymer at a molecular level as a function of such properties as solubility, filterability, binding strength, and capacity. Parameters under study include metal ion loading, pH, concentration of polymer, speciation of the metal ion, and ionic strength.

Status/Accomplishments. Base polymers are being prepared. We are in the process of synthesizing two linear polyethyleneimine polymers, which will allow us to do comparison studies with two of the commercially available polyamines. We are preparing actinide-selective polymers from base polymers. Experiments are under way for optimizing the synthesis of polymers bearing a functional group that will be used in the Am/Pu binding studies.

We began characterization of the actinide selective polymers. We have obtained a viscometer that will allow us to characterize the degree of functionalization of the various polymers. High-performance liquid chromatography has been set up for gel permeation-chromatography analysis. These progressive processes will allow us to determine relative molecular weights for the newly synthesized polymers. We are developing analytical methods on an ion chromatograph (IC) for determining the level of functionalization of the polymers.

Construction of the apparatus for the fluorescence studies is complete. Optic alignment is complete; and we have 80% of the laser power, which is sufficient to perform the fluorescence experiments. The standard operating procedures are written; and we have been inspected by the Los Alamos National Laboratory laser safety team, who enthusiastically approved our system setup.

Core Technology: Separations—Polymer Foams
Principal Investigator: Gordon Jarvinen

Task Description. Our task is to develop advanced microcellular polymer foam materials to replace conventional resin beads in removing nuclear materials and other solutes from processing and waste streams.

Status/Accomplishments. We completed an initial study of the flow properties of chloromethylstyrene foams that had been prepared by various methods. We made 11 types of foams by varying components that affect porosity. We sealed these foams into columns and measured the flow rate of water through the foams as a function of pressure. From these data, we calculated the permeability, densities, and surface areas of each foam.

We found that the type of polymerization initiator used has a large effect on the pore sizes of the foam. An oil-soluble initiator results in larger pores (up to 100 μm in diam). A water-soluble initiator results in pores 10 μm in diam and smaller. We can further control the pore sizes of the oil-soluble initiated foams by using small amounts of salt. The results of changing various parameters are summarized in Table 4.

Table 4. Results of Changing Parameters

Sample	Surfactant Content	Initiator Phase	Salt Na_2SO_4 (g/ℓ)	Density (g/cc)	Flow@5psi (ml/s)	Permeability (darcys)
101A	11%	water	0	0.1023	0.13	0.81
101C	11%	water	0	0.0943	0.06	0.38
102A	22%	water	0	0.1003	0.41	2.47
102B	22%	water	0	0.0866	0.21	1.25
102C	22%	water	0	0.0965	0.35	2.08
102D	22%	water	0	0.0889	0.21	1.28
100-1	22%	oil	0	0.0826	2.1	5.79
112B	22%	oil	0.005	0.08601	0.73	4.37
112A	22%	oil	0.01	0.08437	0.68	4.12
110B	22%	oil	0.05	0.08716	0.29	1.76
110A	22%	oil	0.1	0.08336	0.33	1.96

Permeability was calculated by the equation:

$$F = \frac{K A \Delta P}{\eta L}$$

when F is flow in ml/s, K is permeability in darcys, P is pressure in atm, η is fluid viscosity in cp, L is length in cm, and A is cross section in cm^2.

We functionalized chloromethylstyrene foams with phosphonic acid, using the Arbusov reaction. Initial foams had 2.0–2.7 meq/g phosphonic acid groups (as determined by titration). We also sulfonated the foams, because the hydrophilic environment created by the sulfonic acid groups enhances access to the active regions of the foam. Sulfonation levels, ranging from 2.1 to 4.2 meq/g have been achieved. We will compare phosphonated foams, with and without sulfonation, for actinide uptake.

Flow studies indicate a slight increase in permeability of sulfonated foams in 0.1N HCl and 0.1N NaOH, as opposed to a neutral water flow. The permeability increased from 3.19 to 3.78 for HCl and 3.19 to 3.42 for NaOH.

In preparation for actinide removal experiments, we are working to optimize the performance of a new atomic absorption spectrometer for doing analysis on uranium uptake studies.

Core Technology: Materials Science—Thermodynamics
Principal Investigator: Mark A. Williamson

Task Description. The objective of the thermodynamics task is to study, by both experiment and theory, the phase behavior and thermodynamic properties of plutonium oxychloride, a potential by-product of the plutonium oxidation step of the salt-distillation process.

Status/Accomplishments. During the third quarter, we completed several mass spectrometer calibration procedures. The mass scale of the mass spectrometer was calibrated with perfluorotributylamine, so that the expression for the relationship between mass and dc voltage could be established. In addition, we investigated the sensitivity of the mass spectrometer by studying the vaporization of uranium tetrafluoride. Discrepancies in the uranium tetrafluoride data require a second set of sensitivity calibration experiments. We will complete these experiments after we do our plutonium oxychloride studies. Vaporization studies with plutonium oxychloride will be initiated July 5, 1996. We continue to prepare the report on the phase behavior of plutonium oxychloride.

Core Technology: Materials Science—Vitrification
Principal Investigator: Gerald Veazey

Task Description. The primary objective of this project is to install and demonstrate a glovebox-scale vitrification process that can be used to study the application of vitrification as an alternative to cementation.

Status/Accomplishments. We established performance specifications for waste forms. The physical performance standards that we will use to develop the glass-frit formulation with surrogate wastes will include the following:

- viscosity: 2–10 Pa s at 1150°C;
- electrical conductivity: 18–50 Siemens / m at 1150°C;
- durability: to pass the Savannah River Product Consistency Test (ASTM C1285-94); and
- redox: redox potential to be slightly reduced to prevent metal precipitation. (This reduction will be important if a melt technique involving electrical conductivity is chosen for the full-scale melter. Precipitation can result in short-circuiting.)

Other restrictions will be imposed as necessary for Waste Isolation Pilot Plant (WIPP) storage and transportation. The waste form also will be required to pass the Environmental Protection Agency total concentrate leachate procedure for metals covered by the Resources Conservation and Recovery Act. The waste form must be categorized as nonmixed waste. Currently, no WIPP requirement exists for restricting mixed waste, but interim storage is much less costly for nonmixed waste.

The major concerns with placing vitrification equipment inside the glovebox system were those associated with off-gas treatment and high temperature. The vitrification system will require an off-gas system to remove the NO_x and other volatile components that may be a part of the waste streams being vitrified. The off-gas system required to satisfy this need will be composed of a condenser and a caustic scrubber. The temperature concern involves preventing the heat generated from the vitrification process from damaging the glovebox gloves or setting off the heat sensors in the glovebox. We determined that the hottest exposed area of the resistance heater to be used in this project reaches <50°C. This temperature is well below the 140°–150°C ceiling imposed on furnaces used in the gloveboxes at the Los Alamos National Laboratory Plutonium Facility (TA-55).

Deciding on the optimum system for production-scale operations will not be a goal of this project. Instead, we will use a simple small-scale melter design that will allow data to be collected, with vitrification technology, on the compatibility of various waste streams. These data can be used at a later time to evaluate and select a production-scale system for work-off of 94-1 wastes.

The melter for this project will be a resistance (clam-shell) heater capable of raising the temperature to the 1150°C required for melting borosilicate-based glass. Melting will be done in batch fashion inside a 310 stainless steel (SS), schedule-10, 5-in. nominal pipe melt container measuring 8 in. high. This container diameter will enable convection currents to accomplish the mixing, thus removing the need for an internal stirrer. Another factor in choosing this diameter was that it is the largest nominal pipe size that will fit within the Rocky Flats Environmental Technology Site pipe component for WIPP storage. The pipe component is being proposed as a container that will allow a criticality limit of 2800-g per TRUPACT-II WIPP transportation overpack instead of the present 320 g. This restriction on Fissile Gram Equivalent permitted in a WIPP drum will allow loading of each drum to the 200-g-per-drum criticality limit.

We have made progress on regulatory tasks. We have submitted the environment, safety, and health questionnaire for soliciting comments on potential safety and regulatory issues for the experiments with radioactive materials. We have initiated the request for approval for operation with radioactive materials in accordance with the National Environmental Policy Act. The Los Alamos Environment, Safety, and Health Division's Hazardous and Solid Waste Group has determined, using published state guidance, that the work with radioactive materials can be conducted as a treatability study.

We completed a needed statement of work for the Pacific Northwest National Laboratory (PNNL) project to develop the glass-frit formulation for the evaporator bottoms waste and sent it to PNNL for review. We have almost completed the characterization of the Los Alamos evaporator bottoms waste that is needed for the PNNL work.

During the fourth quarter of FY96, we will begin work with nonradioactive materials that involves high-fired ash. PNNL has supplied Los Alamos with the glass frit developed for this type of waste. We have also acquired most of the equipment to perform the vitrification. Only the off-gas system for the experiments with nonradioactive materials remains to be completed.

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545